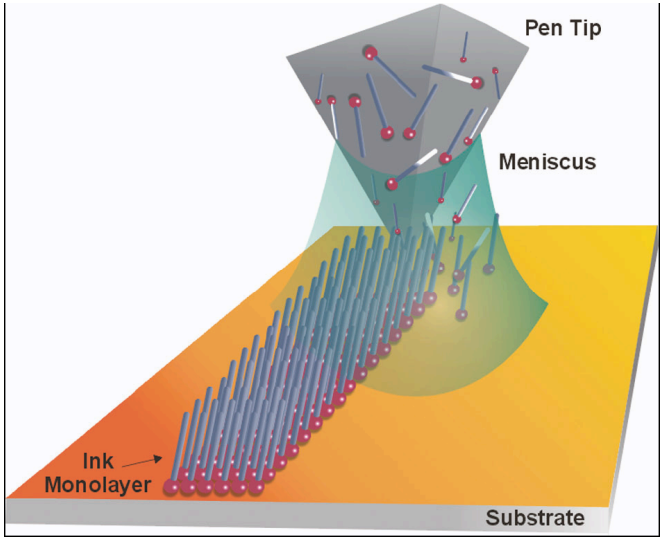
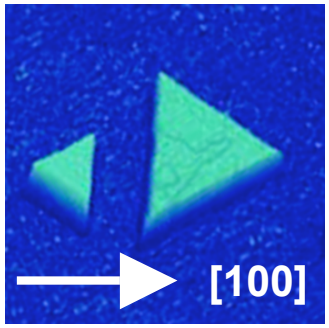
Characterization of Poly-DL-Lysine hydrobromide single crystals grown using dip-pen nanolithography

X. Liu, Y. Zhang, D. K. Goswami, J. S. Okasinski, K. Salaita, P. Sun, M. J. Bedzyk, C. A. Mirkin, *Science* **307**, 1763-1766 (2005).





- **Growth of PLH by DPN on mica(001)**
- **X-ray scattering structural measurements**
  - Back reflection Laue at NU X-Ray Lab
  - Grazing incidence oscillation X-ray diffraction at APS
    - Grazing incidence X-ray diffraction (GIXD)
    - Rotating crystal method
    - X-ray fluorescence (XRF)

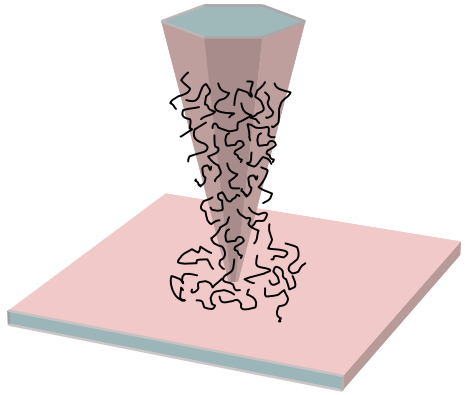
DPN as tool to grow nanocrystal

Solution:

Poly-DL-Lysine-HBr in H_2O (2 mg/μl)

Surface:

Freshly-cleaved mica (001)



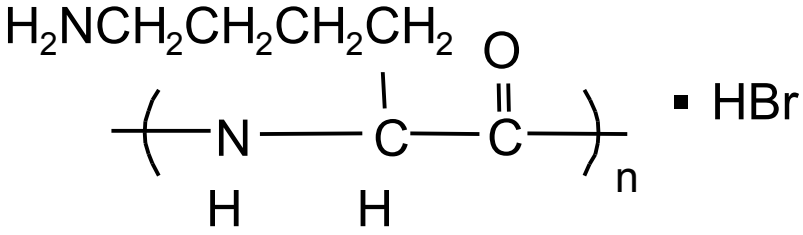
PLH coated AFM tip in tapping mode

Random-Block Co-Polymer does not crystallize from bulk solution

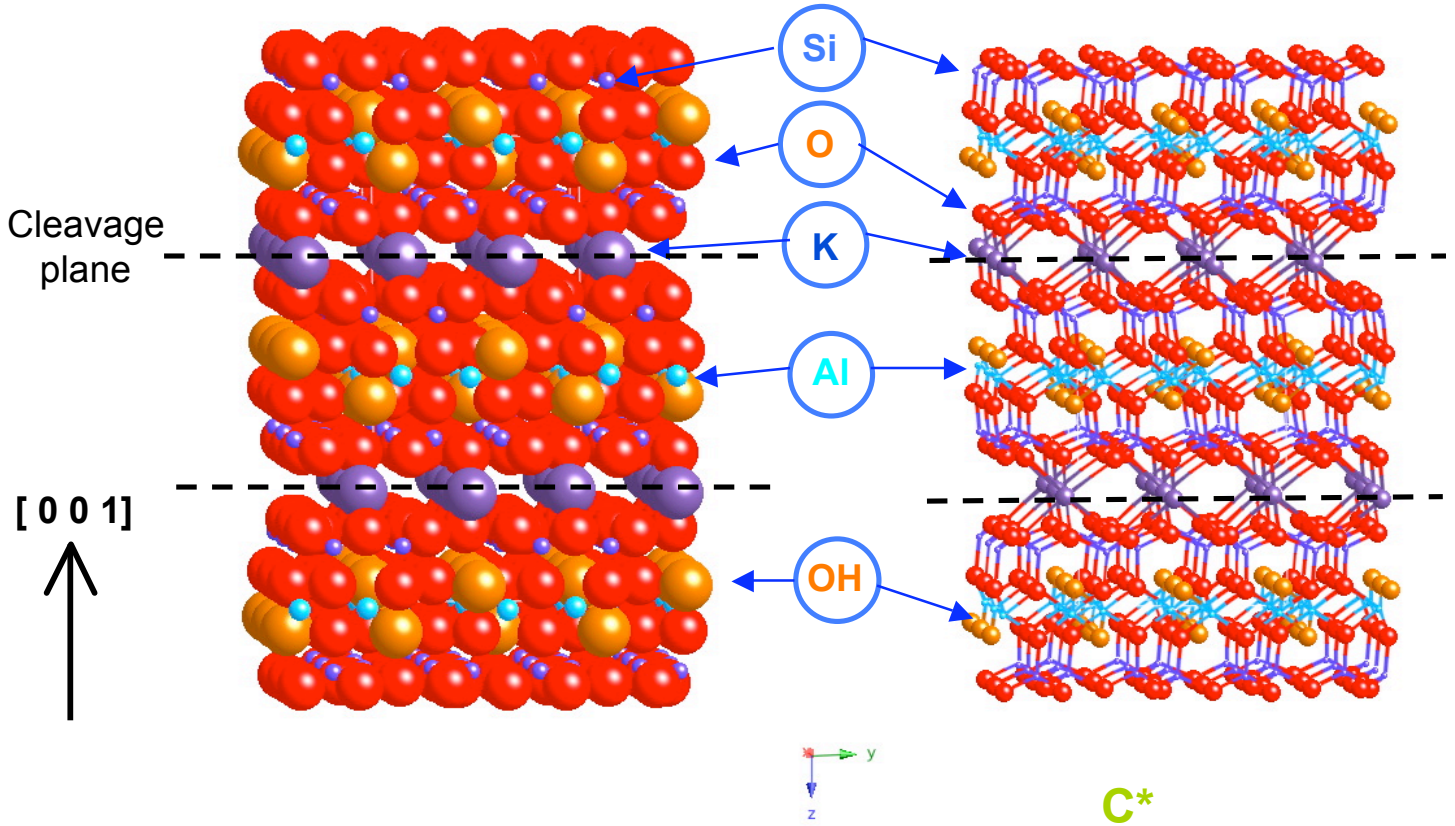
Poly-DL-Lysine hydrobromide (PLH)

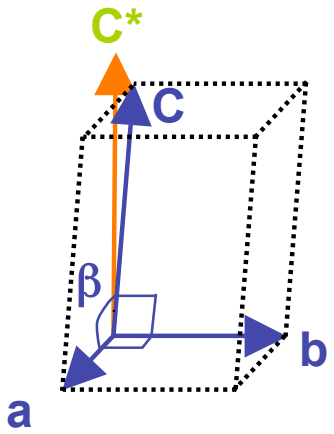
Molecular weight = 4000

L_{min} ~ 6 nm



Mica (001) – $2M_1$ Muscovite [$KAl_2(AlSi_3)O_{10}(OH)_2$]



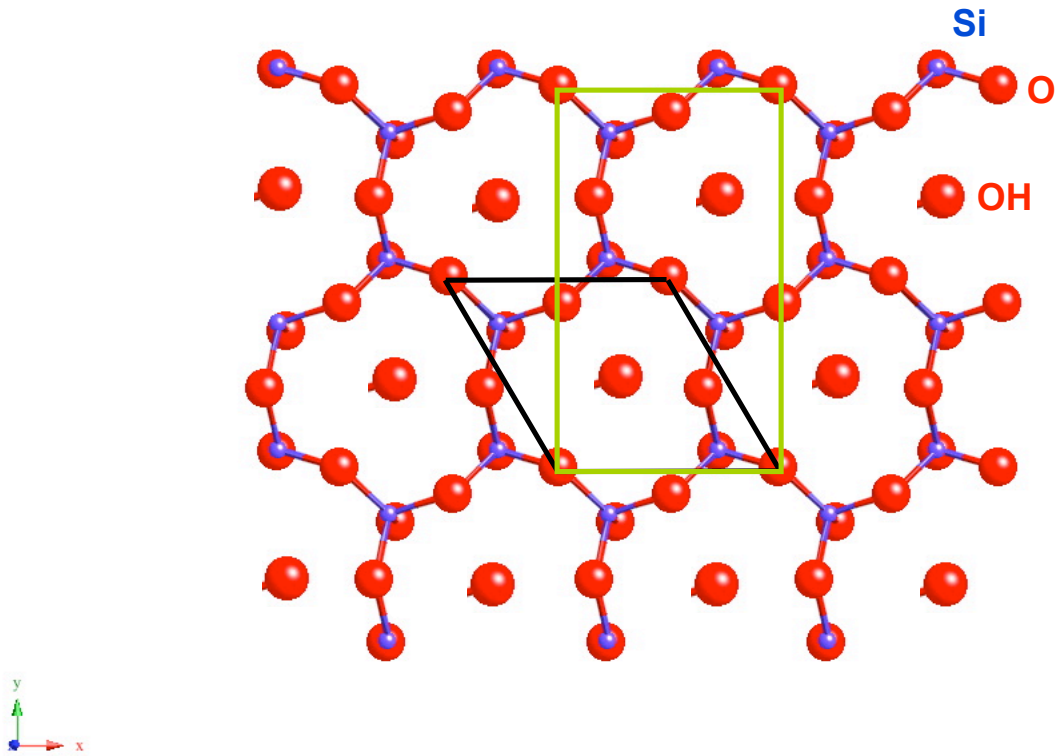


For monoclinic Mica

a = 5.189 Å
b = 9.004 Å
c = 20.256 Å
β= 95.74°
α = γ = 90°

Oxygen Terminating Layer on Mica (001) Surface

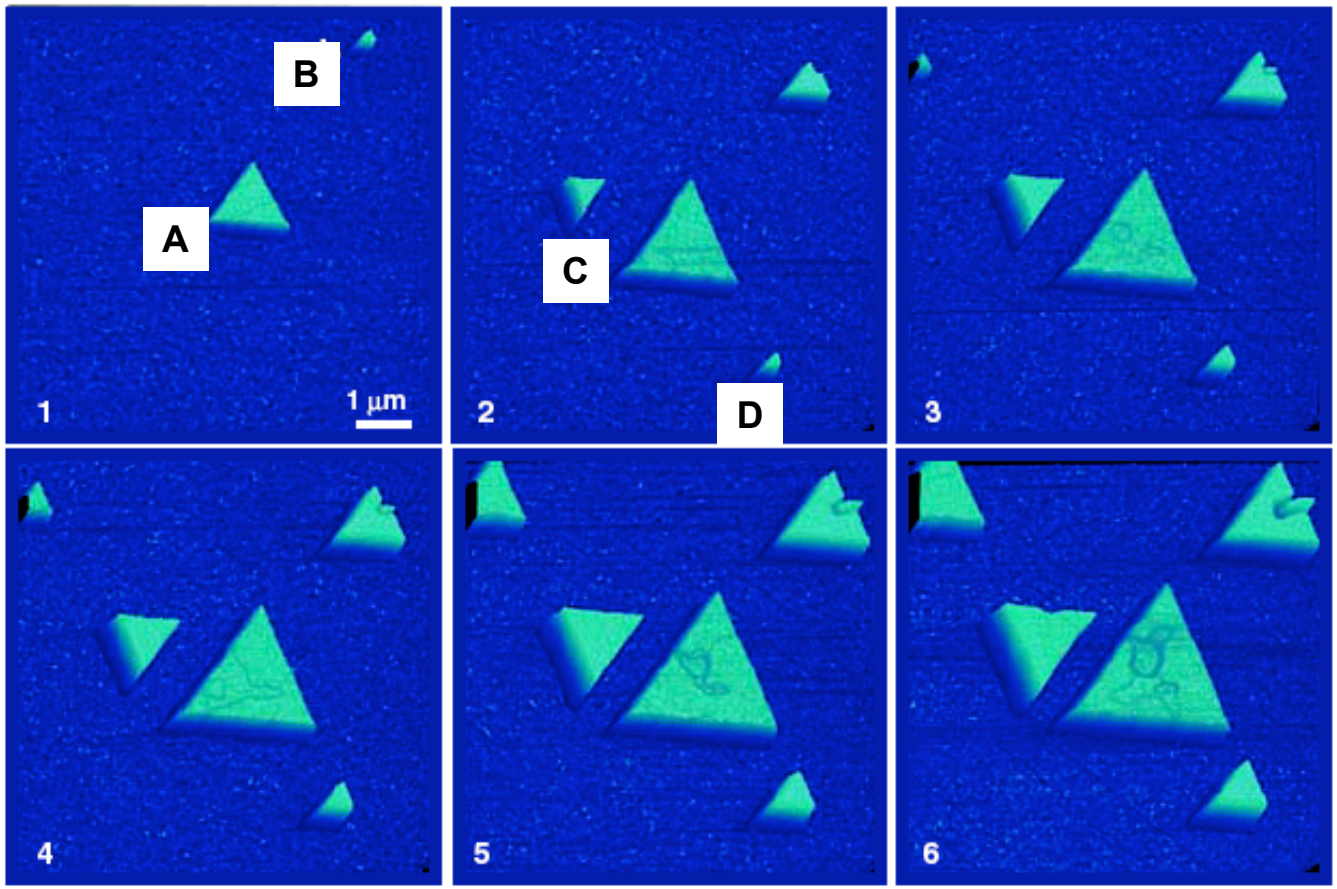
after K^+ layer has been removed by cleavage



Si_2O_3 forms 2D Pseudo Hexagonal Unit Cell

The true unit cell is Oblique with a = 5.189 Å, b = 5.192 Å, γ = 119.980°

A series of AFM images (8x8 μm²) showing the evolution of PLH prisms



- PLH triangles with edge lengths ranging from 100 nm to 10 μm with height from 5 to 50 nm.
- The images have been collected in 256 sec interval
- Relative humidity 30%
- Temperature ~ 20°C

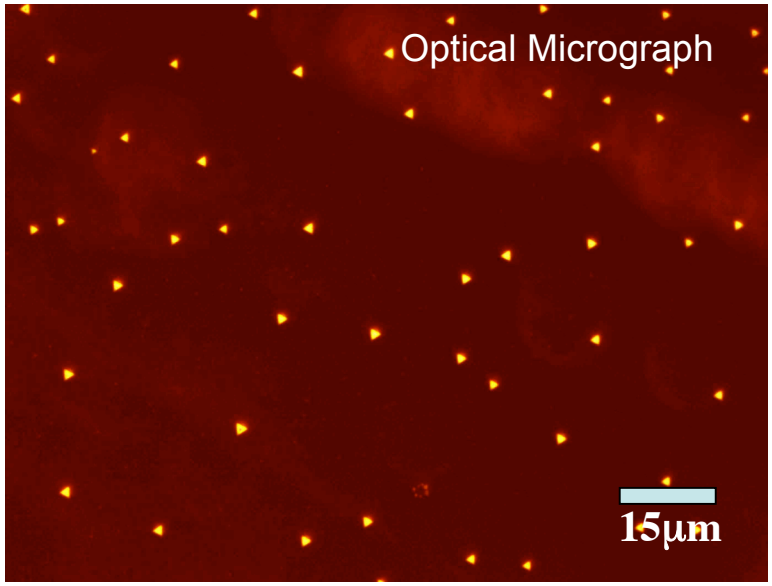
Observations: Nucleation and Growth

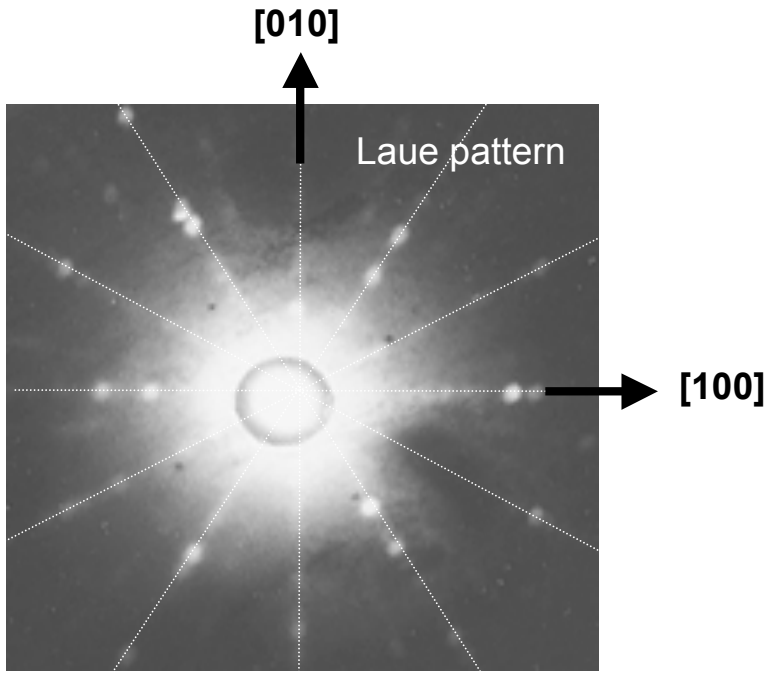
- PLH molecules grow as prisms on mica(001) surfaces
- Equilateral triangles point in one of two opposing directions.

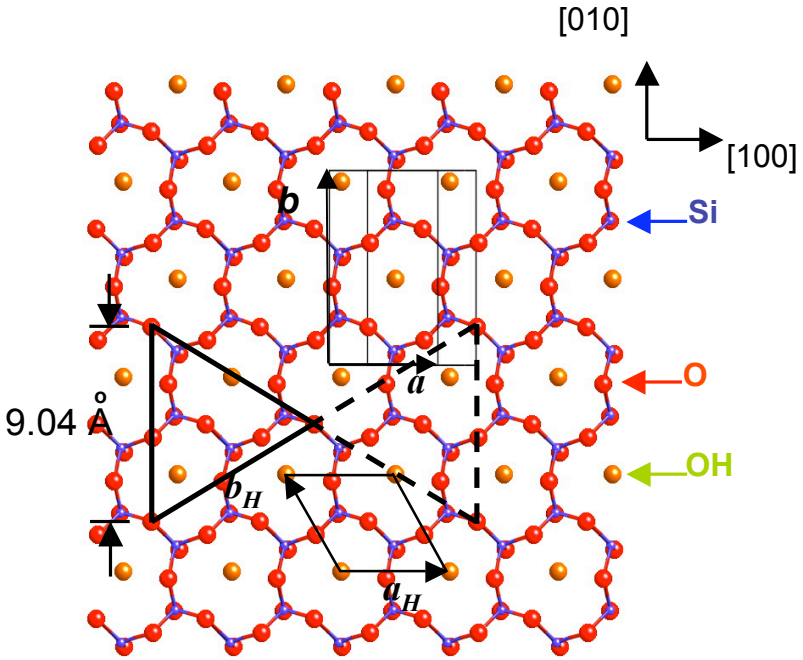
What is this direction relative to mica xtal axis?

Are the PLH prisms single xtal?

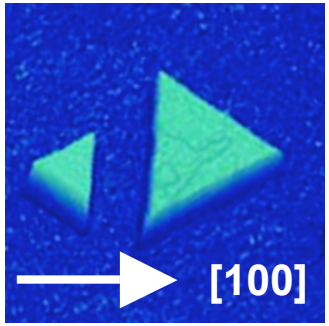
X-ray Back reflection Laue of mica with optical micrograph of triangle prisms:







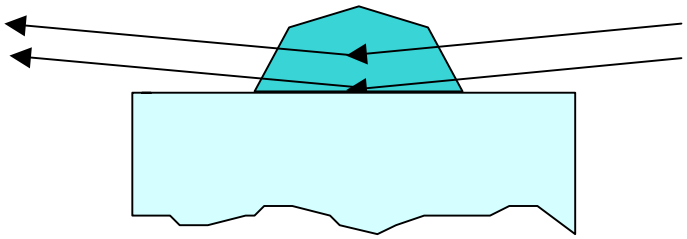
Mica(001) surface



Back reflection Laue revealed that the prisms grow along the [100] direction of mica (001) surface

Grazing incidence oscillation X-ray diffraction method at APS / DND / 5ID-C:

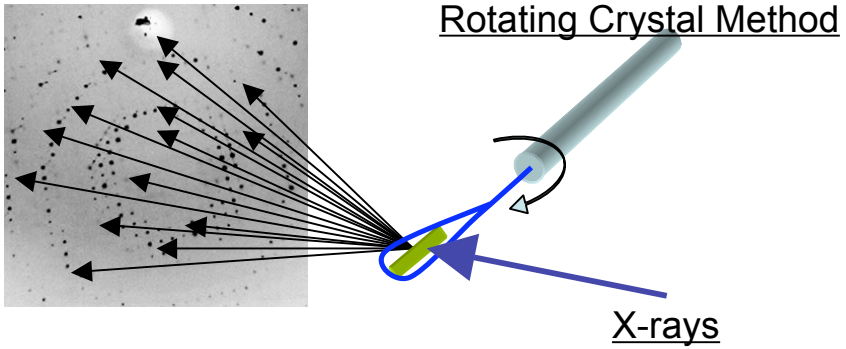
grazing incidence geometry

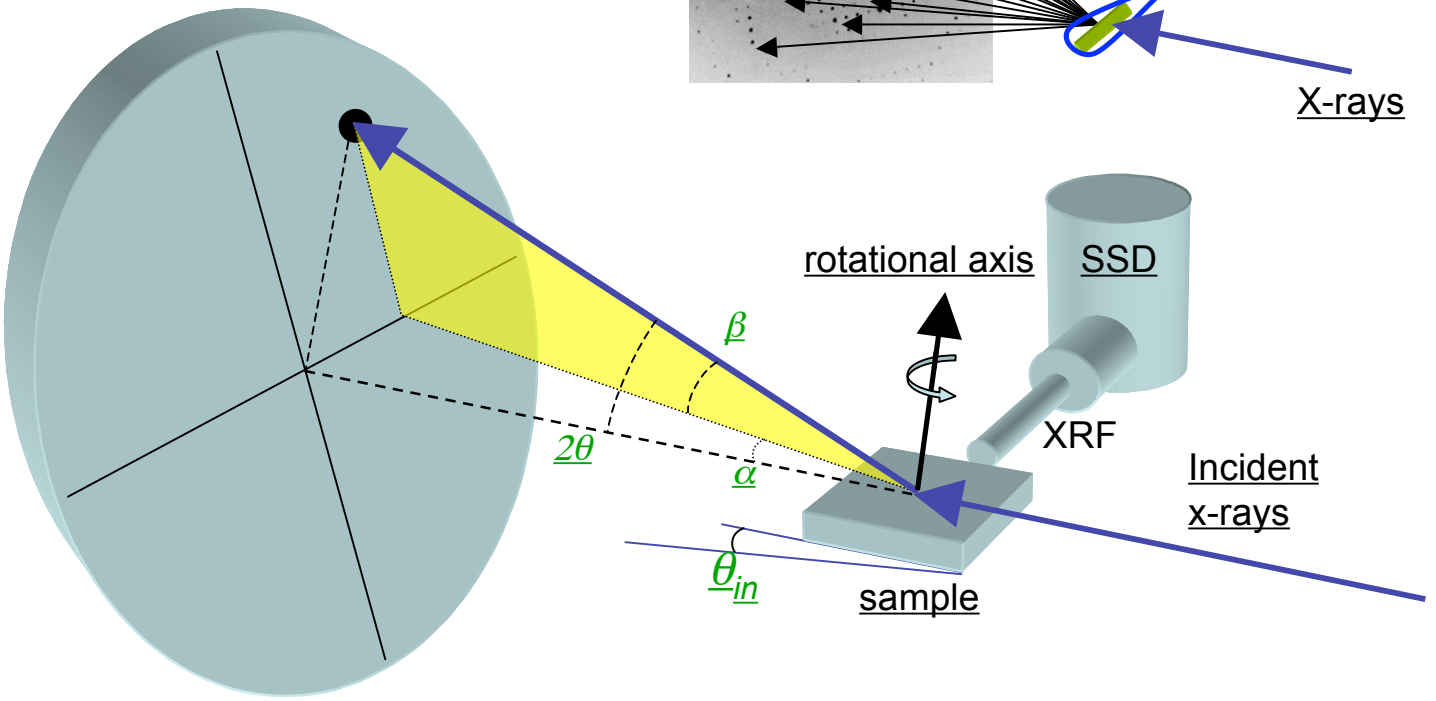


highly surface sensitive

Combined technique:

- Grazing incidence X-ray diffraction (GIXD)
- Rotating crystal method
- X-ray Fluorescence (XRF)

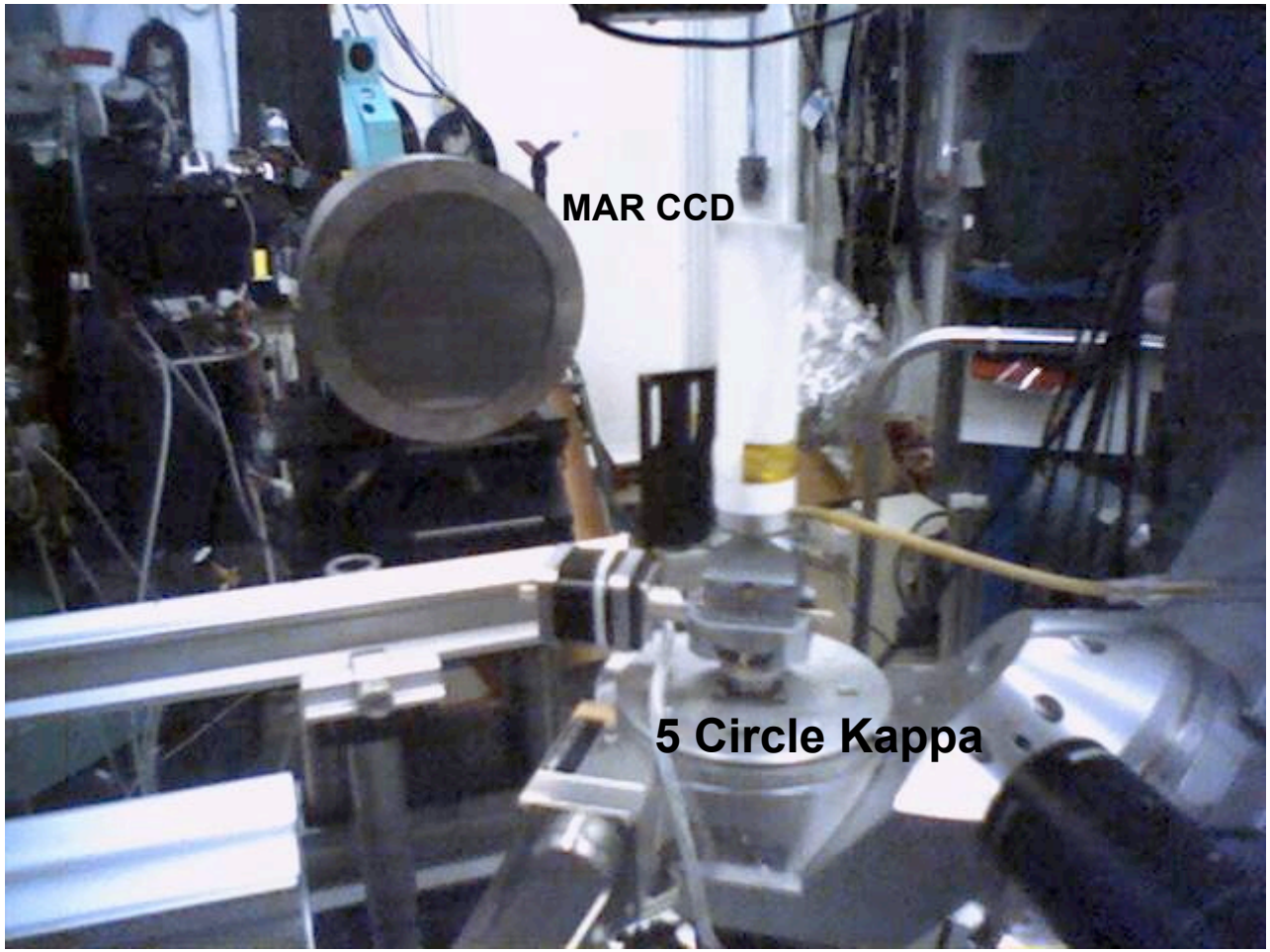




2D CCD Detector

Advanced Photon Source, Argonne, DND CAT, Sector 5, 5ID-C Station

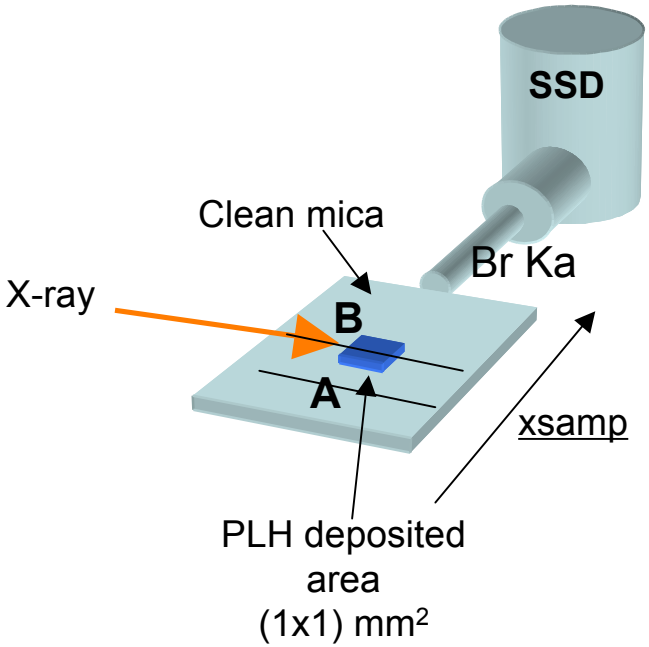
(5 circle Kappa Diffractometer with MAR CCD detector)

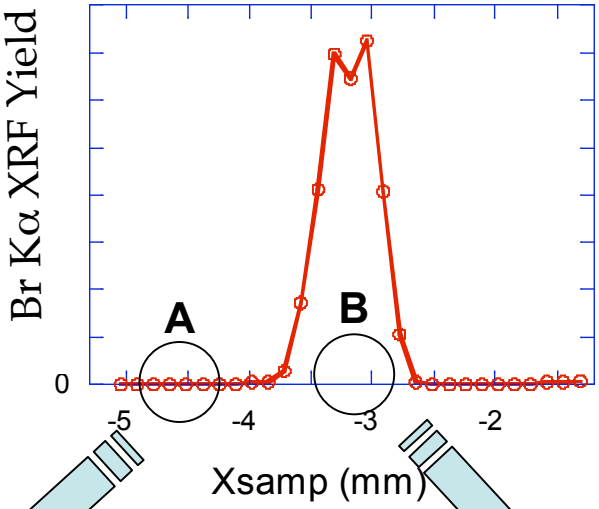


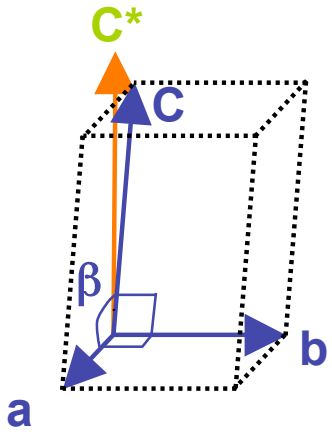
Grazing incidence oscillation diffraction set up

Identifying diffraction spots from PLH prisms:

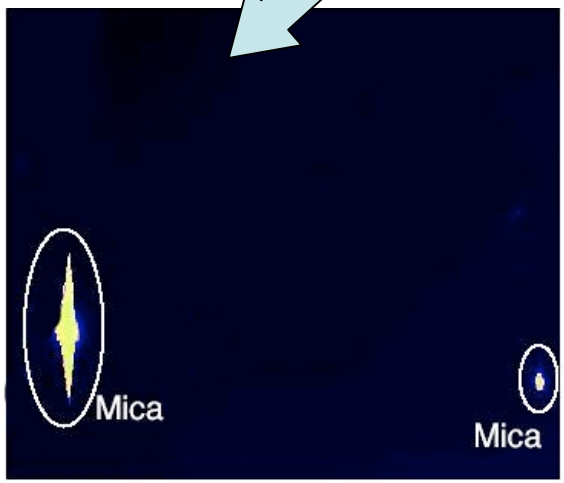
- Br in PLH molecules used as marker
- mica **c*** axis was used as rotational axis
- Two identical oscillations were collected at A and B position at 50° range in ϕ
- Each image was taken over 1° range in ϕ

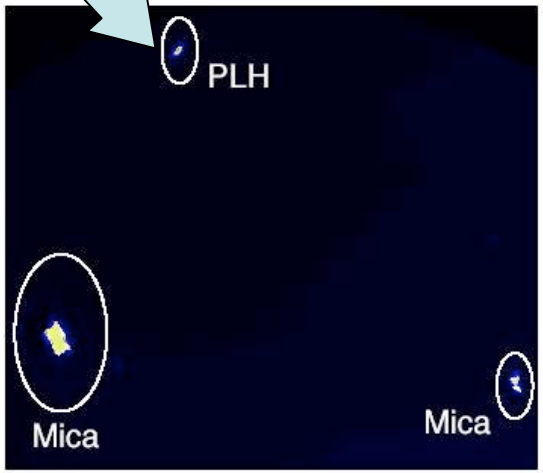






Rotational axis was
Along the c* axis



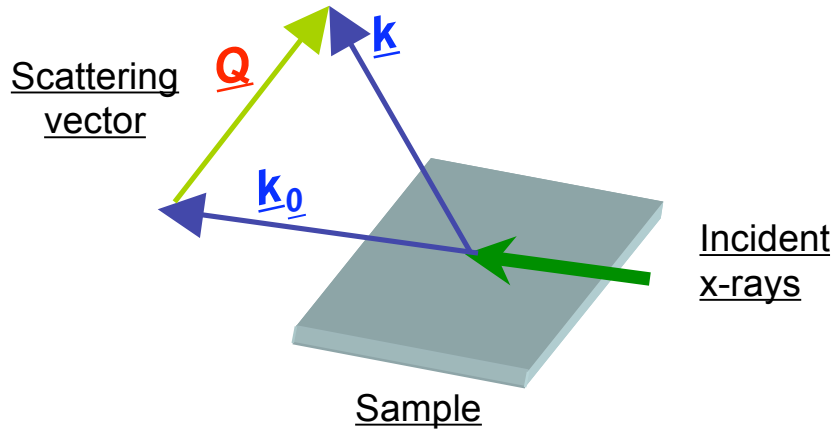


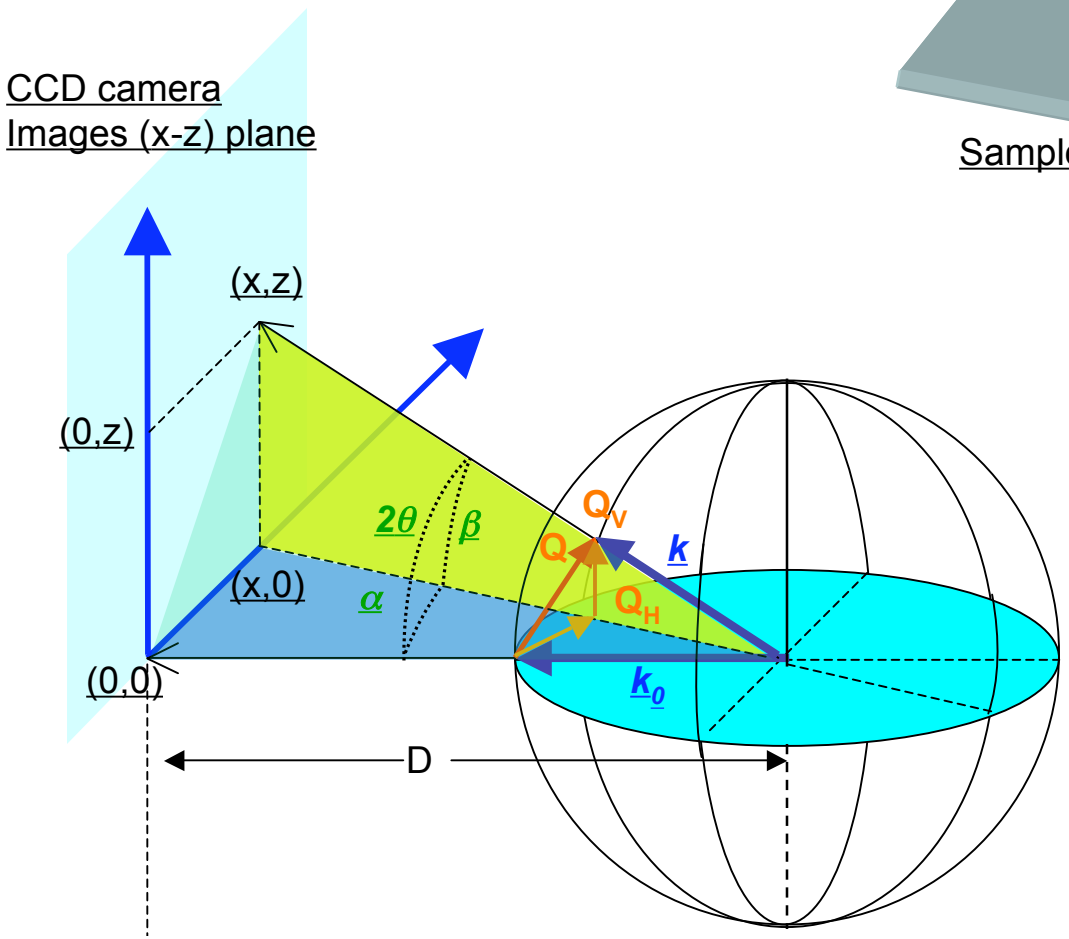
Scattering vector calculation from (x,z) coordinate of the diffraction spots of the CCD images:

$$Q_V = 2\pi/\lambda \sin\beta = {}^{2\pi}/_{\lambda}\,(z/(D^2+x^2+z^2)^{1/2})$$

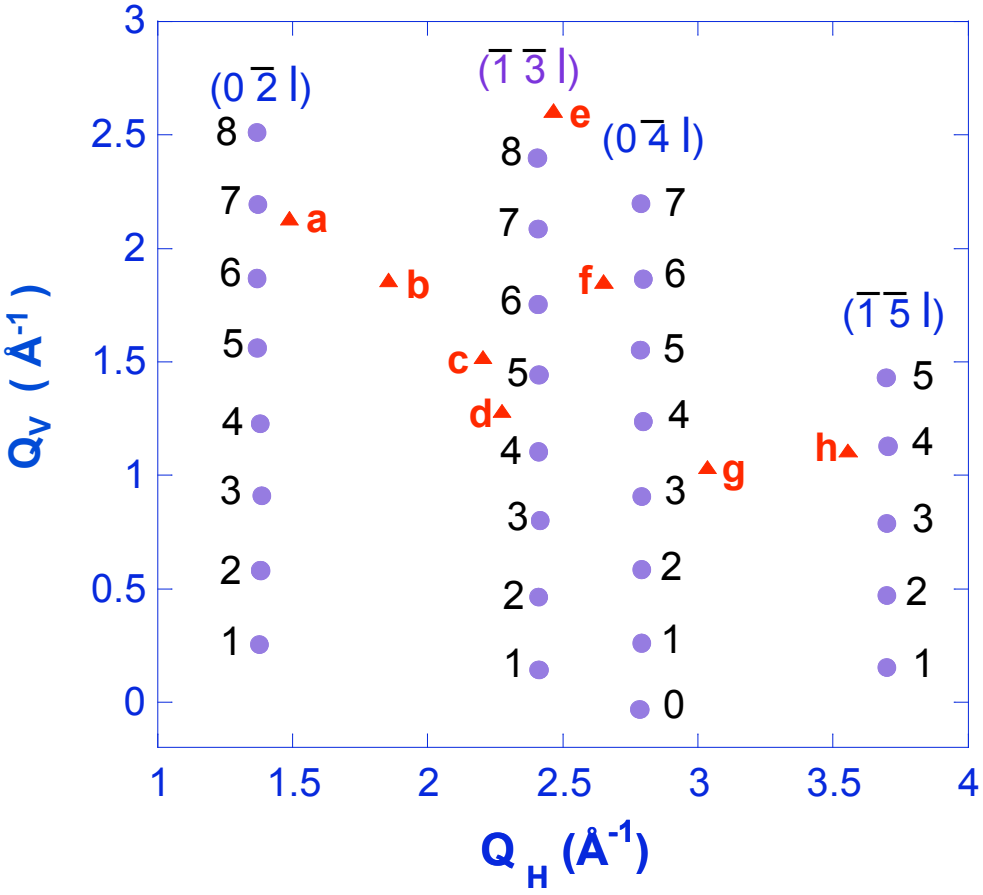
$$Q_H = {}^{2\pi}/_{\lambda}\,[2(1-\cos\alpha\cos\beta) - \sin^2\beta]^{1/2},$$
$$Q_x = {}^{2\pi}/_{\lambda}\sin\alpha\cos\beta, \quad Q_y = -{}^{2\pi}/_{\lambda}\,[1-\cos\alpha\cos\beta],$$
$$\text{And } \cos 2\theta = \cos\alpha\cos\beta = D/(D^2+x^2+z^2)^{1/2}$$

$$Q_H = 2\pi/\lambda\,[2(1- D/(D^2+x^2+z^2)^{1/2}) - z^2/(D^2+x^2+z^2)\,]^{1/2}$$





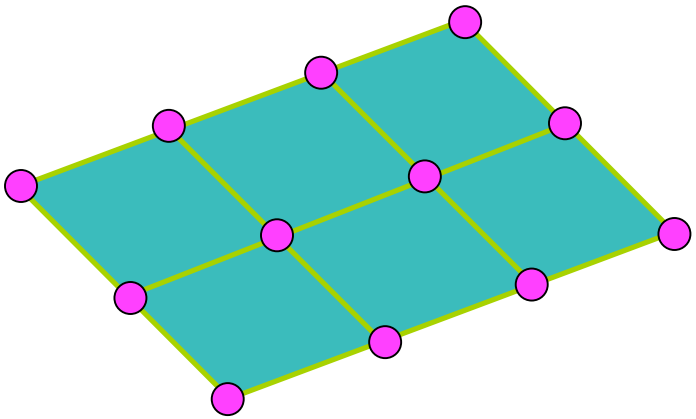
Grazing incidence oscillation X- ray diffraction results:



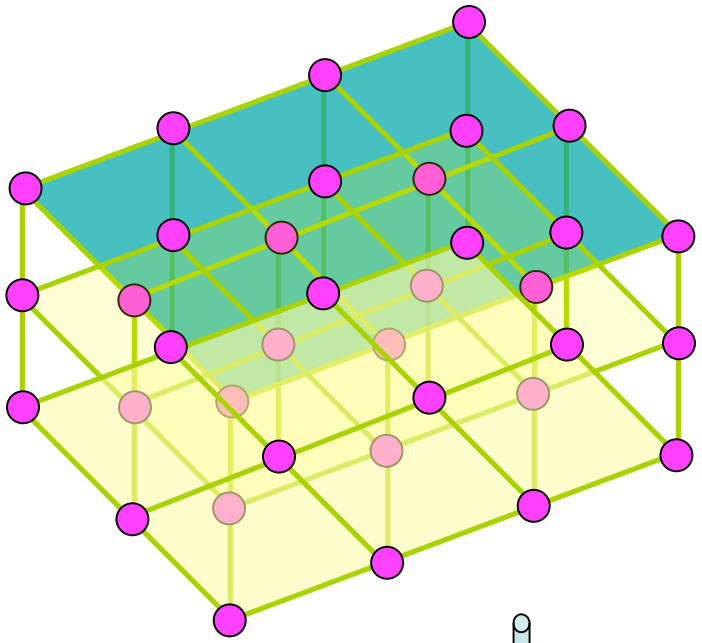
- Q_H and Q_V are the horizontal and vertical components of the scattering vector (**Q**) directly calculated from (x,z) spot coordinate.
- Mica diffraction spots are represented by filled circles PLH diffraction spots are represented by filled triangles
- Mica peaks from each reciprocal rod appearing with same Q_H

Real Space:

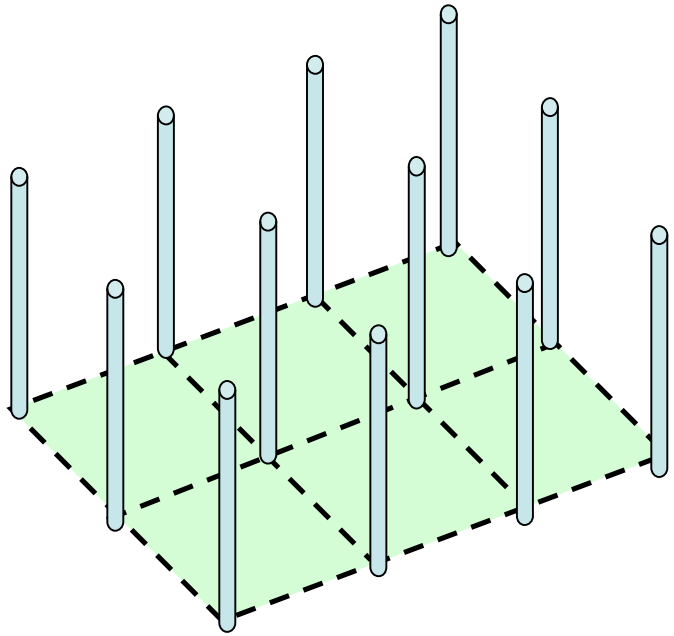
2D layer

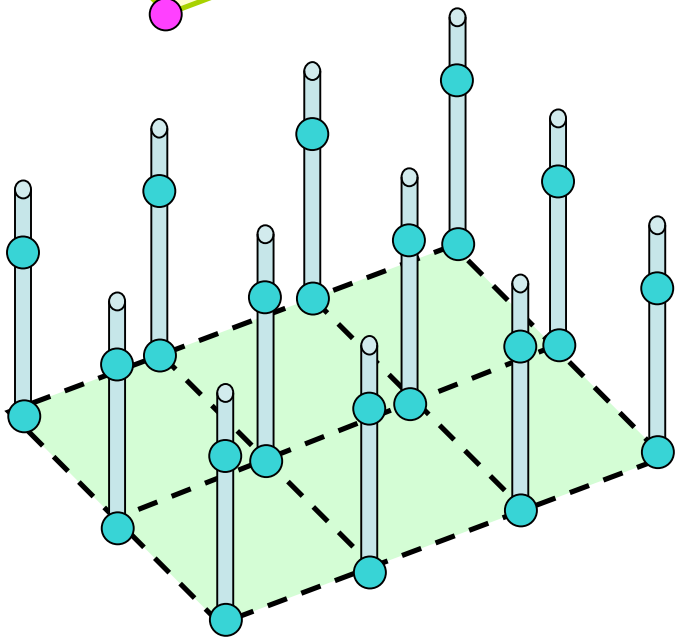


2D layer + Bulk

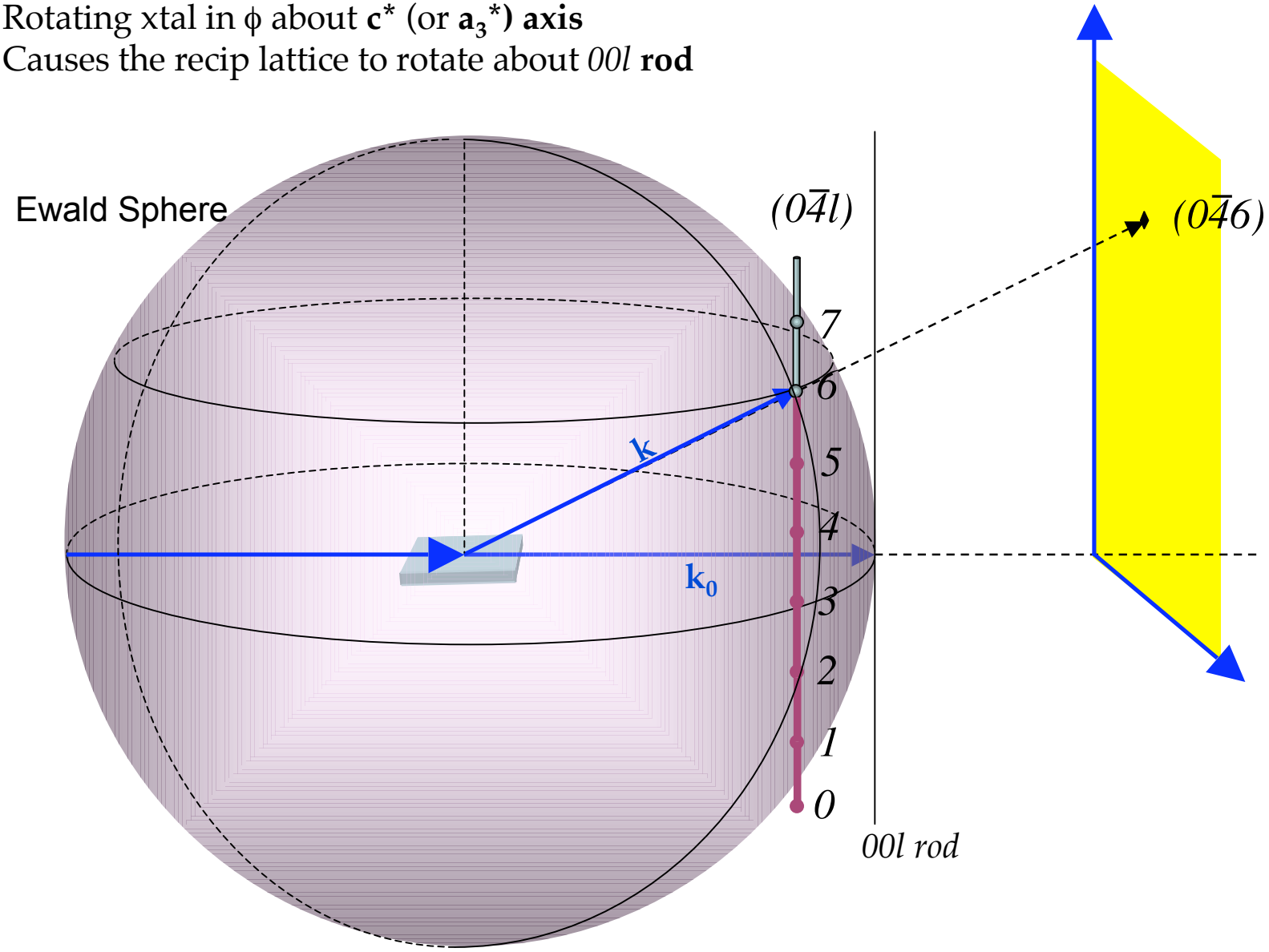


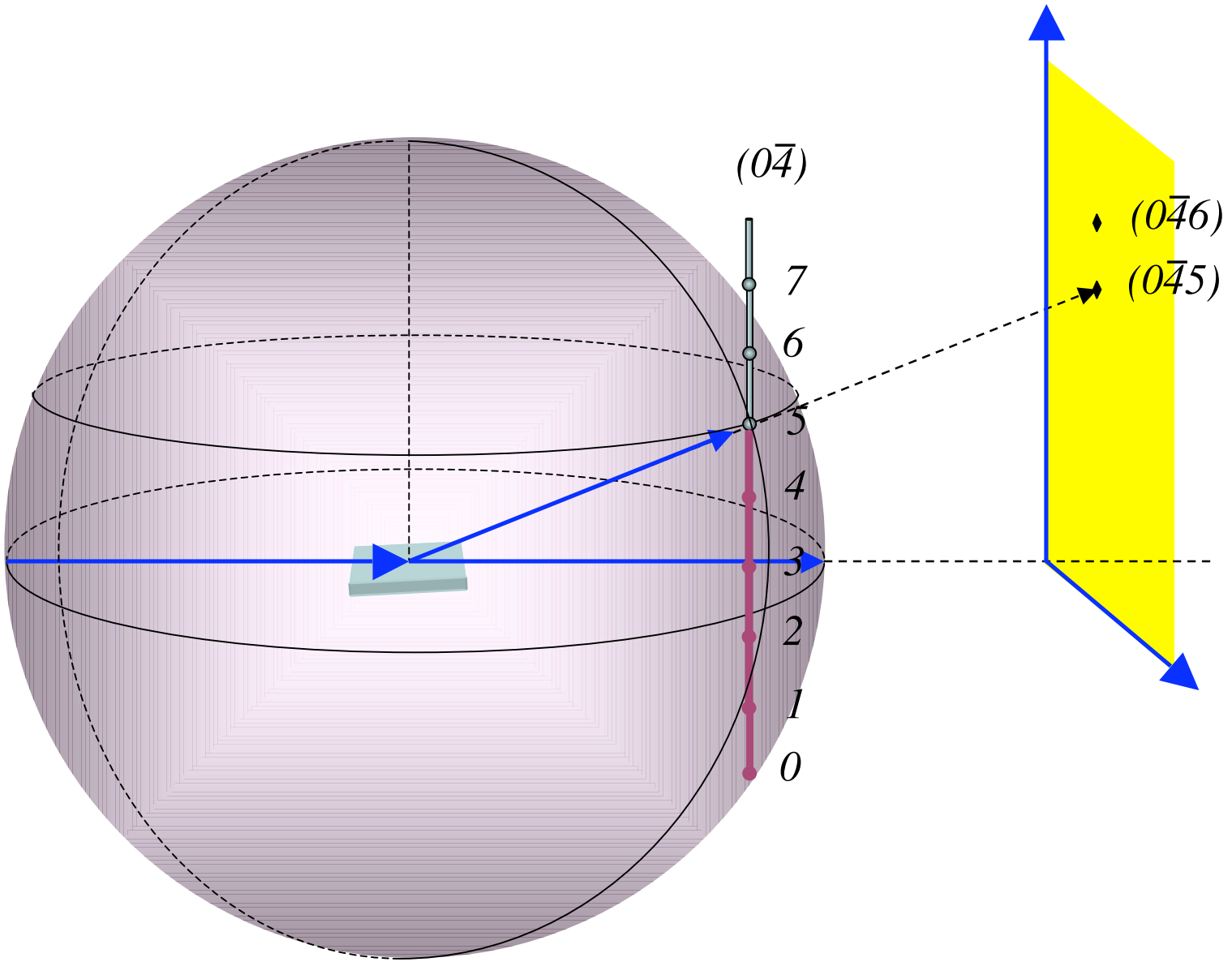
Reciprocal Space:

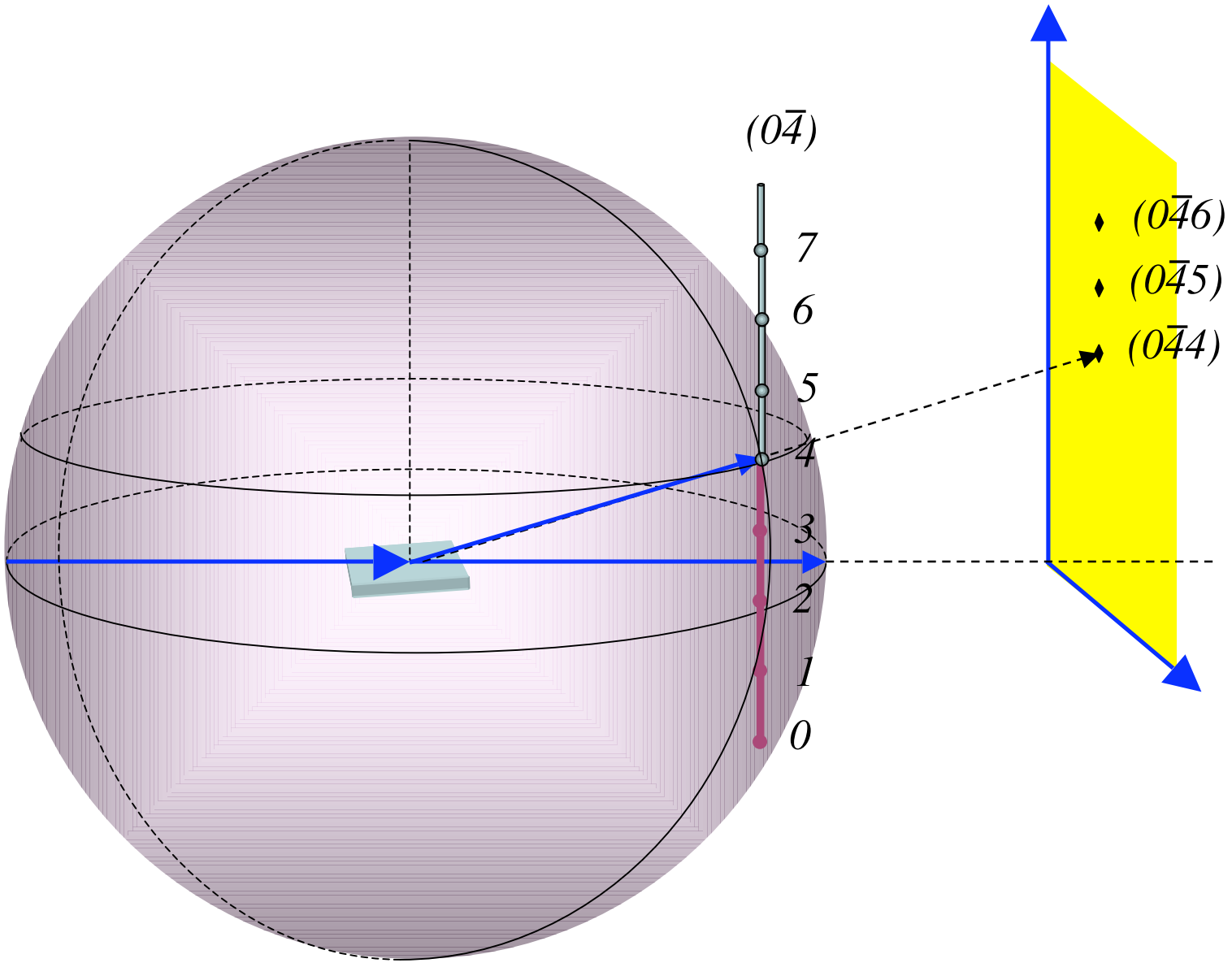


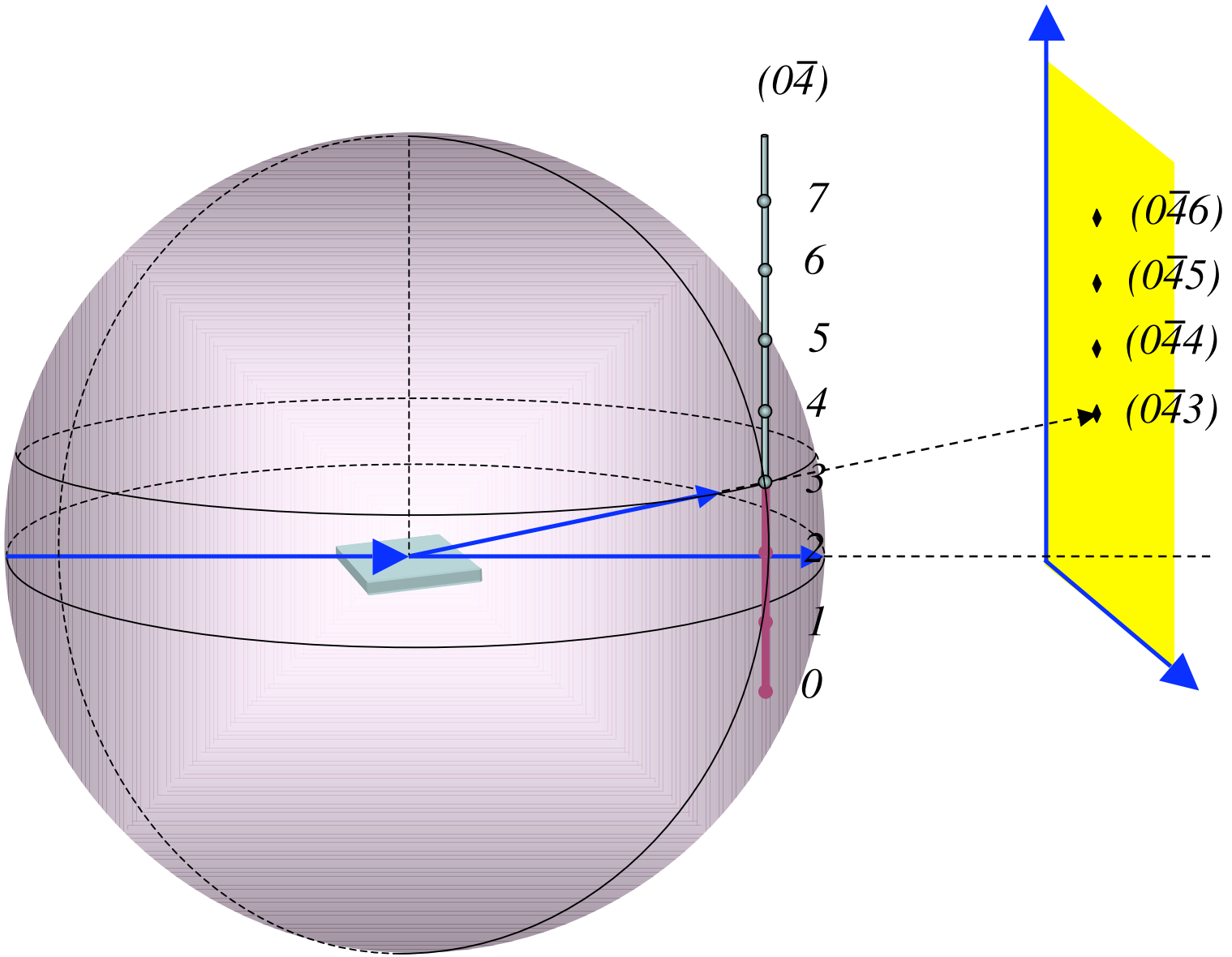


Rotating xtal in ϕ about **c*** (or $\mathbf{a_3}$***) axis**
Causes the recip lattice to rotate about *00l* **rod**

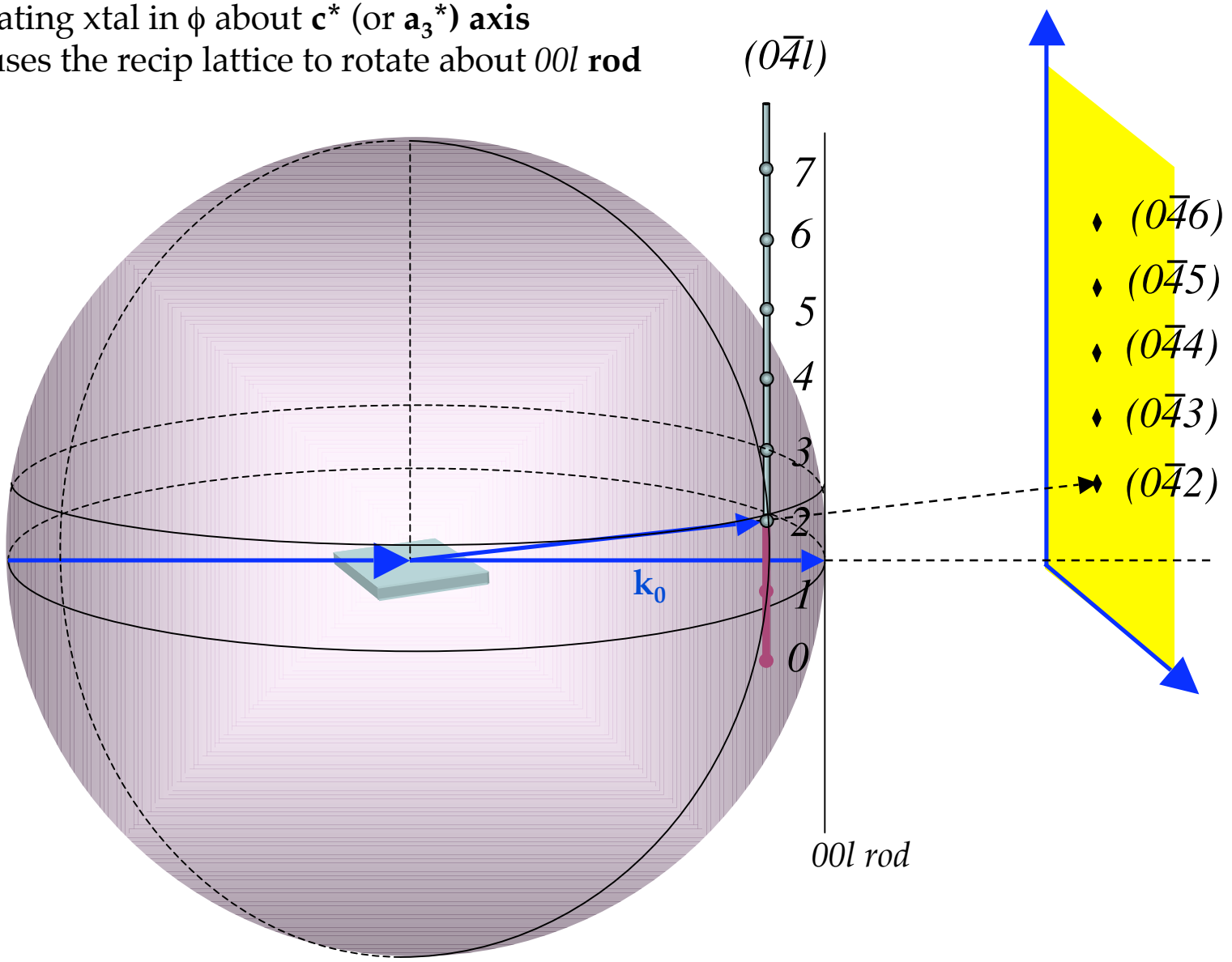



(0$\bar{4}$)
7
6
5
4
3
2
1
0
(0$\bar{4}$6)
(0$\bar{4}$5)


$(0\bar{4})$
7
6
5
4
3
2
1
0
$(0\bar{4}6)$
$(0\bar{4}5)$
$(0\bar{4}4)$


$(0\bar{4})$
7
6
5
4
3
2
1
0
$(0\bar{4}6)$
$(0\bar{4}5)$
$(0\bar{4}4)$
$(0\bar{4}3)$

Rotating xtal in ϕ about **c*** (or **a_3*) axis**
Causes the recip lattice to rotate about *00l* **rod**



Observed azimuth angles (ϕ), relative intensities (I) and d-spacings (d) for the PLH diffraction peaks

Label	ϕ (°)	I	d (Å)	Monoclinic			Hexagonal		
				h	*k*	*l*	*H*	*K*	*L*
A	161	70	2.42	-0.02	-2.31	6.85	-0.02	-1.06	6.84
B	166	38	2.39	0.02	-2.66	5.96	0.02	-1.34	5.97
C	145	32	2.35	-0.69	-2.93	5.15	-0.69	-1.12	4.88
D	163	79	2.41	-0.18	-3.30	4.19	-0.18	-1.56	4.12
E	164	100	1.75	0.17	-3.52	8.30	0.17	-1.85	8.37
F	164	12	1.94	-0.02	-3.80	5.95	-0.02	-1.89	5.94
G	166	99	1.96	-0.03	-4.35	3.33	-0.03	-2.16	3.32
H	148	12	1.69	-0.84	-4.89	3.88	-0.84	-2.03	3.56

Observation from oscillation X-ray diffraction measurement:

- PLH diffraction peaks indices are noninteger and inconsistent with muscovite lattice and therefore originating from the PLH prisms

- Each diffraction spot occurs only at a particular 1° interval of ϕ → indicates prisms grown on mica are single crystal with a lattice that has an in-plane orientational epitaxy with the underling mica lattice .

  Note that this is quite different from the previous case of OPV-Silicate spin coated on glass, where the occurrence of diffraction spots was independent of ϕ.